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Accumulation of absorbed fly ash particulate matter and its impact on the CC process

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Abstract

Fly ash entering a CO_2 capture plant in the incoming coal-fired flue gas is a potential source of metals which support as catalysts the formation of degradation products in the MEA solvent. This study presents an assessment of the accumulation of absorbed particulate matter and an evaluation of the impact on the CC process. The particulate matter which is absorbed inside the CC plant and the ratio of flue gas flow to the installed liquid inventory determine the rate of accumulation. Filtration or settlement of particulate matter inside the process does not avoid leaching. The results of one ash sample from an European power station are presented leached with fresh 30 wt% lean MEA at different ratios (1:10 to 1:2000 g/g, ash/solvent) The results show that mobility of the trace elements Cu, V, Mn increases significantly to lower ash concentrations compared to the Fe mobility values. Dissolved Fe concentrations of 0.5-1.0 mg/L derive from leached fly ash after approximately 500 hours of operation provided that 1 mg/m ³ is absorbed and a high ratio of flue gas flow to liquid inventory is installed. Small dissolved Fe concentrations might still trigger the formation of degradation products.

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Keywords: CO_2 Capture, Fly Ash, Coal Flue Gas, Accumulation, Enrichment factor, Leaching, Mobility of elements;

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1. Introduction

Amine based Carbon Capture (CC) pilot plants behind coal-fired power stations partly absorb fly ash particulate matter which is still available in the flue gas at the end of the conventional flue gas cleaning process. This absorption takes place in spite of the presence of electrostatic precipitator (ESP) or a baghouse for reducing the amount of particulate matter and an additional wet scrubbing in the flue gas desulfurization system (FGD. In case of German coal-fired power plants the emission of particulate matter is usually limited to 20 mg/Nm³ (dry, 6 % O_2).

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Due to the cyclic nature of the process and a fixed solvent volume in a typical CC plant, absorbed fly ash particles are enriched over time. Heavy metals like Fe, Cu and Mn are leached from the accumulated particulate matter and can act as catalysts for the oxidative degradation of typical CC solvents such as 5 M MEA solvent (Goff, ref. 1). Unterberger et al. (ref. 2) postulated a degradation product based corrosion cycle which includes heavy metal concentrations e.g. Fe, Cr and Ni ions for the catalytic enhancement of MEA oxidation.Therefore the thorough understanding of the impact of fly ash is critical for the evaluation of pilot plant results and the design of demonstration plants for CC technology to operate on coal fired power plants.

The effect of particulate matter in the flue gas of coal-fired power stations on amine based CC process has, to date, not been studied in much detail beyond initial investigations. The focus on testing of different solvents and the superficially low amount of particulate matter entering the CC pilot plants might be the reasons.

A previous laboratory study (ref. 3) demonstrated that fly ash particulate matter undergoes leaching with fresh lean and rich MEA solution to some extent. Higher leaching rates are observed in the rich solvent at lower pH compared to lean solvent. Degraded MEA solutions from two different CC pilot plants were then subjected to similar testing (ref. 4) demonstrating that operational solvent degradation increases the solubility for V, Cu significantly, but only slightly for Fe.

Da Silva et al. (ref. 5) have demonstrated that the ESP ash of a coal-fired power station at a ratio of approx. 1:300 (g/g, ash to solvent) increased the formation of degradation products at 55 °C. Chandan et al. (ref. 6) investigated the impact on degradation products at 80 °C with a ratio of 1:100 (g/g) for 5 different ESP ashes which revealed an ash specific influence that was not characterised further.

This study focuses on the time dependent accumulation of fly ash particulate matter in CC pilot plants operating with 5 M MEA and the related mobility of metals, e.g. Fe from absorbed fly ash material. The accumulation of fly ash particles inside the solvent depends on the particulate matter concentration upstream the absorber, the flue gas flow to be treated, the operational time, the liquid inventory, and the capture rate of the particulate matter.

In order to evaluate the leaching effect the ratio of ash to liquid in g/g is considered and the influence of the flue gas flow per volume of liquid inventory, which has a dimension of a space velocity (h-1), is calculated and evaluated for the amount of metals, e.g. Fe, which can be leached under those conditions.

Laboratory experiments have been also undertaken, which are based on fresh 30 wt% lean MEA solvent with ratios of 1:50 and 1:500 (g/g) of added ESP ash from a coal fired power station, to simulate the time dependent enrichment of fly ash material inside a CC plant running with 5 M MEA, and to confirm the concentration level of metals, e.g. Fe, which can be considered for the evaluation.

2. Materials and Methods

As for previous work, it is assumed that ESP ash is an acceptable proxy for studying the effects of particulate matter on the capture solvent (ref. 3)

A spot sample of the ESP ash from a known power station (referred here as PP3) have been taken from the total flow of captured ESP ash to the storage silo using standard internal methods. The average particle size of the samples was much lower than 10 mm, the maximum size acceptable for standard leaching tests. The composition of ash was characterized by X-ray Fluorescence (XRF). To ensure good quality spectra a portion of each ESP ash sample was pressed into a 40 mm tablet using a wax binder before characterization. The concentrations of the main and minor compounds and heavy metals were determined quantitatively. The results for the main compounds are calculated as oxides (as is standard for ash characterization).

Leaching tests on the ESP ash samples were conducted according to the European Standard EN-12457-4 at room temperature using a rotary shaker [7]. For 24 hours of leaching the ratio of solid to liquid varied between 1:10 (g/g)

to 1:2000 (g/g) in order to determine the mobility of Fe in dependence of the ash to liquid ratio. In contrast for 96 hours an experiment was conducted to recognize the difference of the leaching when fly ash is exposed with a certain ratio of 1:50 or 1:500 (g/g) for the complete time of 96 h parallel to a staged dosage of 1:200 or 1:2000 (g/g) every 24 hours.

Leachates were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) for heavy metals. For the leaching tests, a solution of 30 wt% (5 M) MEA (delivered as 99.5% purity, Merck KGaA) in demineralised water and carbonated to lean solvent quality was used.

3. Results

3.1. Properties of an ESP ash spot sample

The composition of ESP ash is generally site specific and varies over time due to the qualities of the different coal fuel diets and variation in those diets during typical commercial operation of coal-fired power plant. One spot samples of ESP ash from power station PP3 was taken in March, 2015. Whist this is not a representative sample in itself, based on our experience of ash analysis the composition of major & minor compounds and heavy metals is considered usual for ESP ash from hard coal fired power stations in Europe. As shown in Figure 1 the main compounds in this ESP ash sample differ insignificantly to former examinations (ref. 2 and 3).

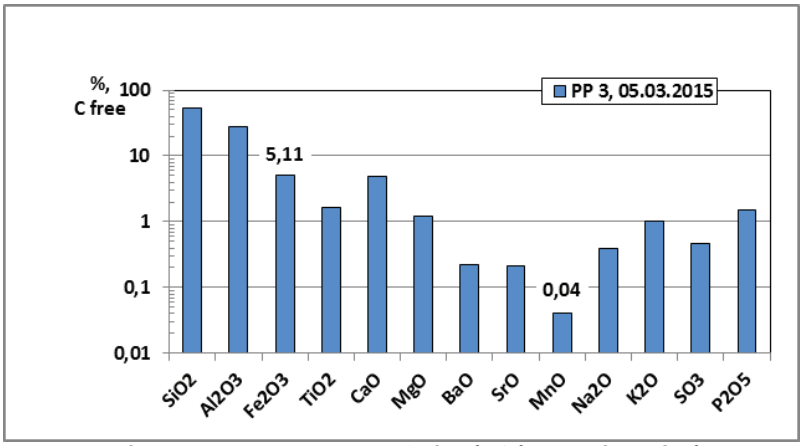

Figure 1. Ash major component composition (carbon free) for ESP ash samples from PP3.

Only surface salts, free lime particles and a portion of the accessible, glass-like surface area undergo dissolution during the leaching tests [ref. 3, ref. 8].

Figure 2 contains the ash trace element concentrations of the ESP spot sample from PP3 taken at 5th of March, 2015. The Mn concentration is found to be somewhat lower than for previous samples, but all the other trace elements match well with previous results.

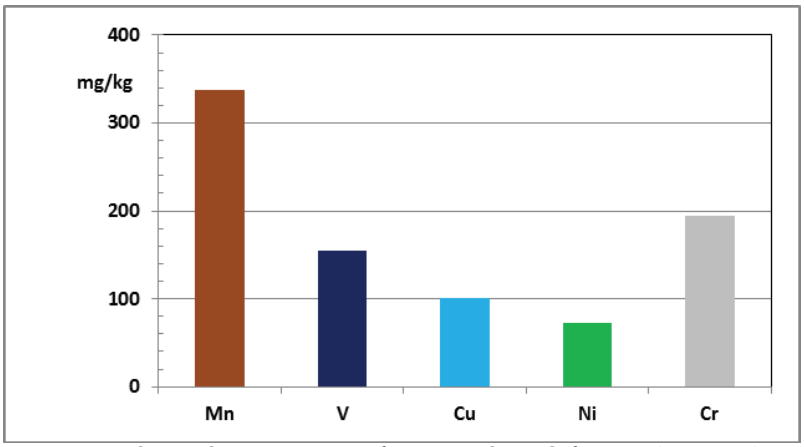

Figure 2. Ash trace element composition for an ESP ash sample from PP3 (05.03.2015).

3.2. Calculations of the accumulated ash content over time

The most important parameter for leaching of ESP ash or fly ash is the ratio of ash to liquid. At the start of operation of any CC plant the ash content of the solvent is zero and there is an increase over time plant specifically.

The concentration of absorbed particulate matter (PM) in the solvent depends on the absorbed particulate matter of the flue gas, the ratio of flue gas flow to solvent inventory and the time:

$$\frac{absorbed\ PM\ [mg]}{solvent\ [L]} = PM_{flue\ gas}\left[\frac{mg}{m^3}\right] \times \frac{\dot{V}_{flue\ gas}\ [\frac{m^3}{h}]}{solvent\ [L]} \times time\ [h]$$

The ratio of flue gas flow in Nm³/h (dry, actual O_2) to solvent inventory (L) is site specific. It has the dimension of a space velocity, a known chemical engineering design parameter. Within the typical CC process the absorption takes place only in the absorber plus wash water section and the absorbed particulate matter is then distributed to the total solvent inventory by circulation and subsequent mixing. Therefore this ratio is better termed a site specific enrichment factor. If the ratio is low for instance between 0.2-0.4 m³/(h x L), then quite a significant volume is installed within the circulation loop which is typical for CC pilot plants. Higher ratios up to approx. 1.0 m³/(h x h) indicate a more compact plant which is expected to be more typical for demonstration and commercial CC plants based on known designs. The higher this ratio is the more rapidly the concentration of particulate will reach a certain concentration level based on the same absorbed particulate concentration from the flue gas flow. Figure 3 shows the dependency of the concentration of particulate matter in the solvent to operational time for a specific enrichment factor of 0.5 m³/(h x L), which is a similar value to that found in a well-studied pilot plant such as to the Castor pilot plant at Esbjerg power station, Denmark.

Two grams of suspended particulate matter per L are reached for an ash input of 1 mg/m³ absorbed and for an enrichment factor of 0.5 m³/(h x L) after 4000 h or for 2 mg/m³ absorbed after 2000 h. 2 g/L ash concentration is equivalent to a ratio of 1:500 (g/g, ash/solvent). Many of the CC pilot plants operate with a direct contact cooler (DCC) directly upstream the absorber, therefore it is very likely that the particulate matter concentration upstream the absorber (after the DCC) is between 0.5-2 mg/m³, because a high capture rate for small particulate matter can be expected due the use of a packed washing system for SO_2 absorption in a typical DCC system.

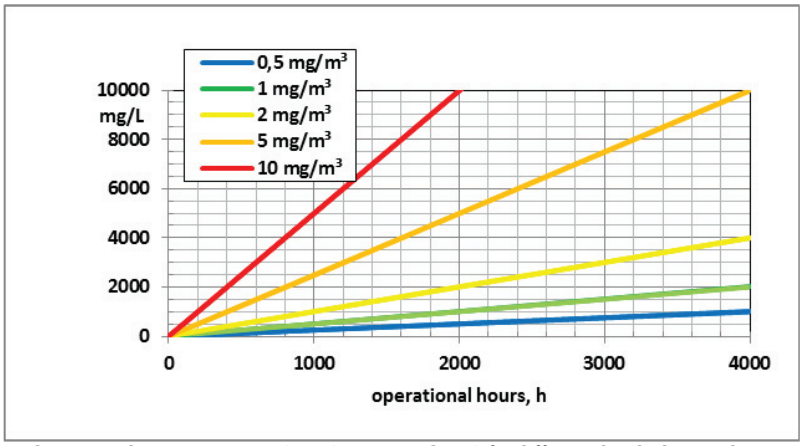

Figure 3. Time dependent particulate concentration (mg/L) at 0.5 m³/(h x L) for different absorbed particulate matter concentrations.

Figure 4 shows samples of different ash to solvent (5 M MEA lean) ratio. All bottles have been rotated in order to distribute the settled ESP ash material through the solvent. At approximately 100 mg/L ESP ash the suspension starts to look cloudy, at 1000 mg/L it looks optically dense. Within a CC pilot plant in operation the MEA solvent did not appear cloudy after 3000-4000 hours. Although it is difficult ascertain because of the changed color. The use of cartridge filter, activated carbon filter and/or settlement within tanks or sumps reduce the amount of particulate matter which remains in the circulated solvent.

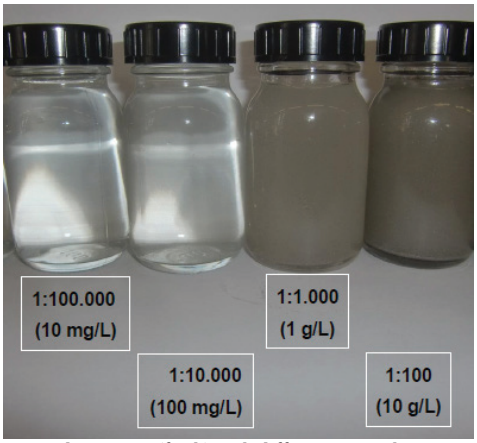

Figure 4. 5 M lean MEA (fresh) with different ESP ash concentrations

3.3. Impact of the ash to liquid ratio on leachate quality (24h/Room Temperature(RT))

The particulate matter is leached to some extent according to the temperature and the loading (rich or lean) in dependence to time. All ESP ashes have in common that that the dependency of the Fe concentration in the leachate to the ESP ash in the solvent is nearly linear between 5 and 100 g ESP ash per L solvent (figure 5, ref. 3). The slopes differ from plant to plant or from time to time of sampling because of the changing quality of the coal or the coal blend, but for lower ESP ash concentrations e.g. 5 g/L the variation due to the different ESP ashes becomes smaller. In figure 6 one example of this dependency of Fe dissolved from the ESP concentration of PP3 is shown with a

logarithmic scale, and in figure 7 with a logarithmic scale for Mn, V, Cu, Mo, Cr and Ni.

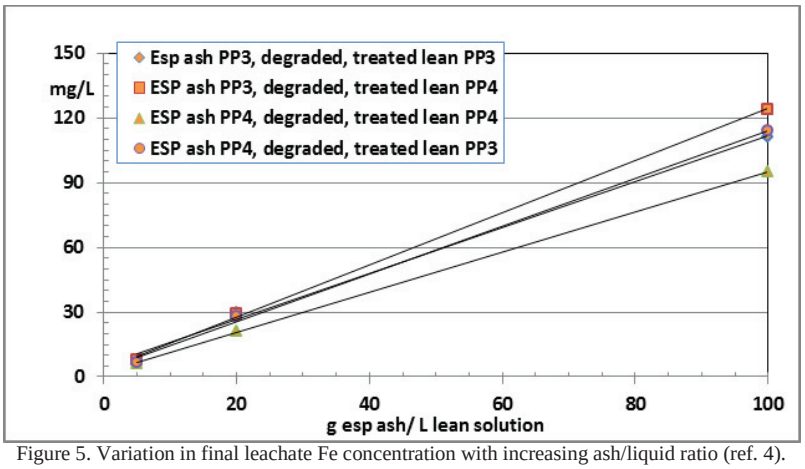

Figure 5. Variation in final leachate Fe concentration with increasing ash/liquid ratio (ref. 4).

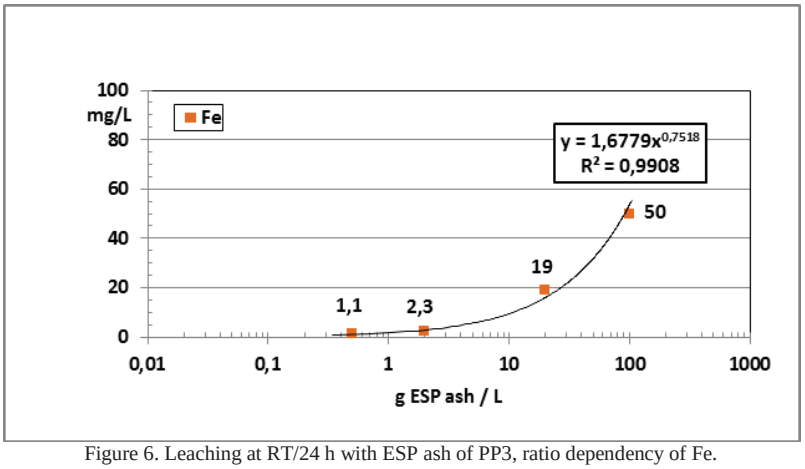

Figure 6. Leaching at RT/24 h with ESP ash of PP3, ratio dependency of Fe.

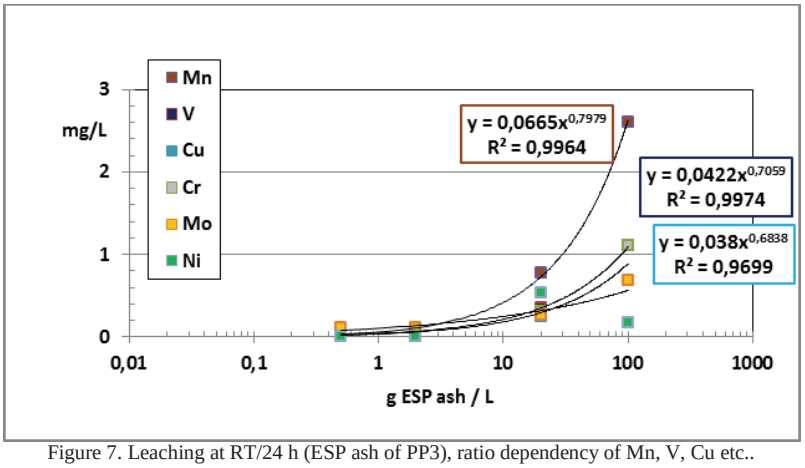

Figure 7. Leaching at RT/24 h (ESP ash of PP3), ratio dependency of Mn, V, Cu etc..

By decreasing the ash to liquid ratio from 1:500 to 1:2000 (g/g) only the Mo concentration remains constant at 0.11 mg/L. Fe reduces from 2.3 mg/L (1:500) to 1.1 mg/L (1:2000). All other analysed heavy metals decrease by approx. 50 %, and all other heavy metal concentrations are lower than 0.05 mg/L at 1:2000 (g/g).

3.4. Calculated mobility values for Fe, Cu, V and Mn at Room Temperature/24 h

The mobility is defined as the ratio of the dissolved mass of the element in the leachate to the total mass of the element in the ESP ash to be leached (ref. 9). As an example the Fe concentration in the leachate of 50 mg/L for 1:10 (g/g) means that 500 mg Fe per kg ESP ash has been dissolved, resulting in a mobility of 1.4 % (as 35,472 mg/kg Fe is present in the ESP ash).

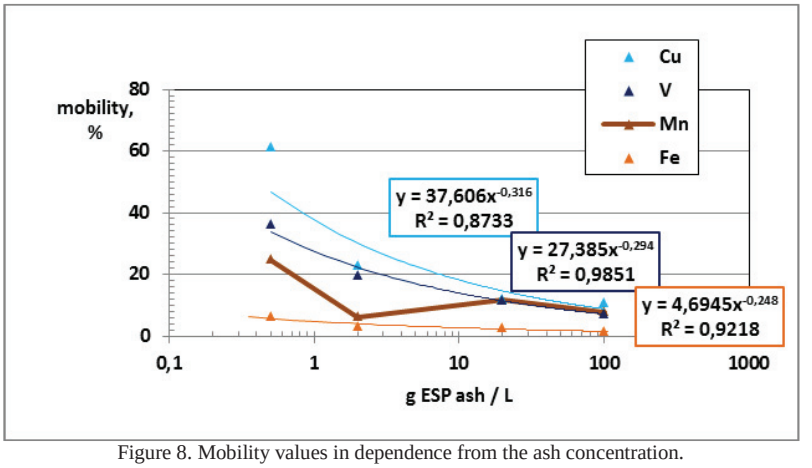

Figure 8. Mobility values in dependence from the ash concentration.

Each heavy metal behaves slightly differently when the mobility values are linked to the ash concentration in the solvent. Generally lower ash concentrations dissolve specifically more heavy metals. Whereas the mobility of Fe slightly increases from 1.4 % at 100 g ESP ash / L to 6.2 % at 0.5 g ESP ash/L, the change in mobility of Cu is more marked, rising from 10.9 % at 100 g ESP ash/L to approx. 60 % at 0.5 g/L. The mobility values for V and Mn also increase significantly, but less markedly than observed for Cu.

For an ash concentration of 0.1 g ESP ash /L even higher mobility values can be expected.

3.5. "Simulation" of continuous absorption of particulate matter by a staged leaching experiment at lab

If a certain ash concentration of the solvent is reached by accumulation for example, 1 g/L, then each mg of the total amount of ash which is absorbed has a different residence time for leaching Fe, Cu, V and Mn from the particulate matter. Assuming a constant flue gas flow, a constant absorption rate and a constant inventory of the solvent, then the average residence time is half of the time which has been necessary to accumulate the ash concentration of 1 g/L. In order to identify if the residence time matters or not, the following leaching experiments were fulfilled. Figure 9 visualizes these lab experiments. In one set leaching with fresh 5 M lean MEA took place for a ratio of 1:50 (g/g) at room temperature (RT) for 96 h without any interruption. In the second set leaching started with 1:200 (g/g) across 24 h/RT with the same solvent. Then the same ESP mass as before was added after 24 h, thus the ratio for the next 24 h of leaching increased to 1:100 (g/g). After 2 additional dosages after 48 and 72 h leaching continued up to 96 h. Both sets leached the same mass of ESP ash, but the leaching time differed between 96 h and 60 h on average. The results of leachate analysis are shown in figure 10. The difference between set 1 and set 2 is small for each element. A second attempt with even lower ash concentrations (1:500/RT/96 h time parallel to 1:2000/RT/24 h plus

3 dosages every 24 h, figure 11) reveals smaller absolute concentrations, but only small differences for each element between both sets. The concentration of Ni was found to be lower than the limit of detection (<0.01 mg/L) for both sets of the second attempt. This leads to the observation that the ash concentration is important for the concentration of the dissolved species, not the time for accumulation.

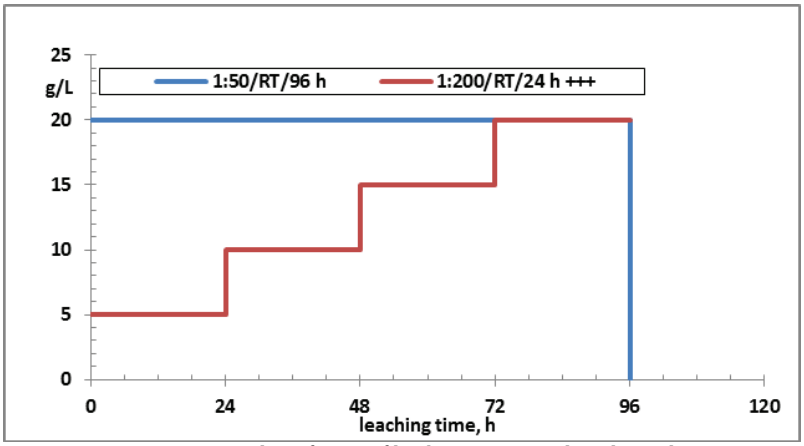

Figure 9. Procedure of 2 sets of leaching, continuously and staged

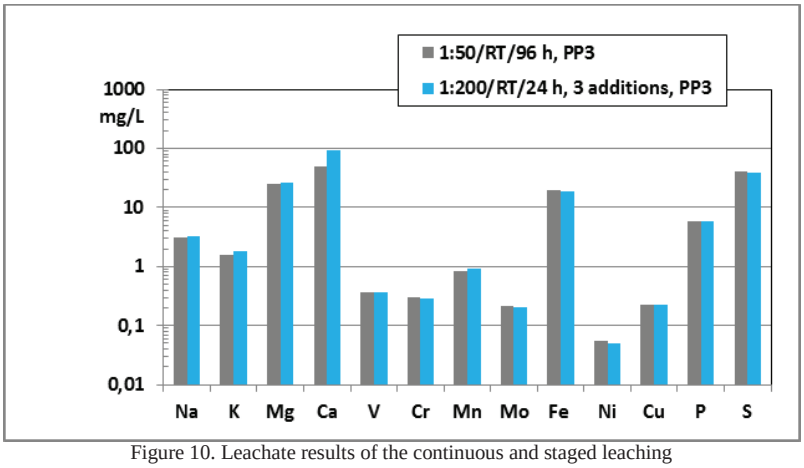

Figure 10. Leachate results of the continuous and staged leaching

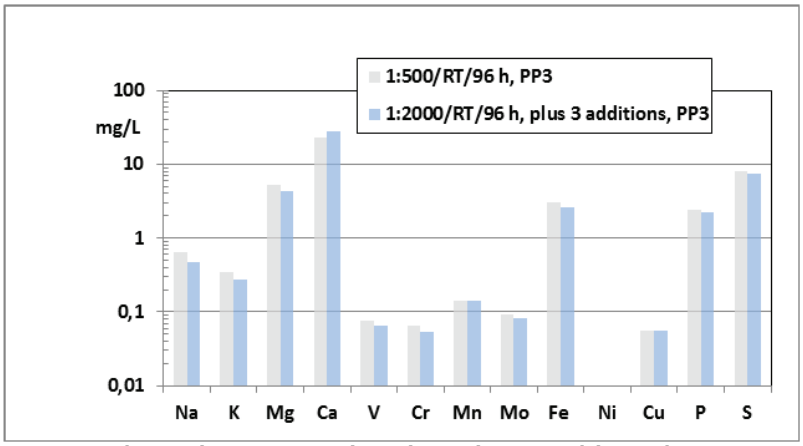

Figure 11. Leachate results, continuous and staged, second attempt with lower ash concentrations.

3.6. Ash/liquid ratio in dependence to the specific enrichment factor

Two other research groups have run tests with added ESP ash to identify their impact on the formation of degradation products. Da Silva et al. (ref. 5) added 3,4 g ESP ash/L rich 5 M MEA solution at 55 °C for approx. 500 hours. Chandan et al. (ref. 6) used 10 g ESP ash/L rich 5 m MEA solution at 80 °C for approx. 150 hours. Although the results cannot be scaled down, these results suggest that at approximately 3 g ESP ash/L an accelerated formation of degradation products occurs. Therefore accumulated ash concentration after 4 different operational times are calculated for several specific enrichment factors 0.1, 0.167 (CC pilot plant Heilbronn, ref. 6), 0.5 (similar to CC pilot plant Castor) and 1.0 $m^3/(h\ *.L)$.

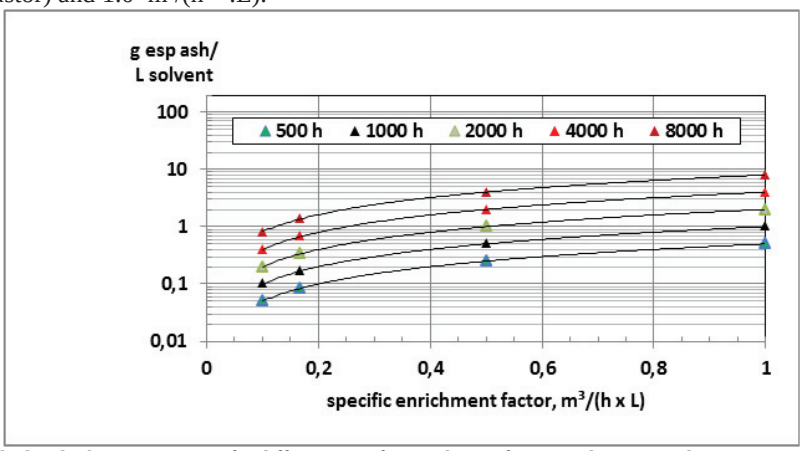

Figure 12. Calculated ash concentrations for different specific enrichment factors and operational time at 1 mg/m³ absorbed.

Figure 12 shows that for a pilot plant with a low specific enrichment factor of 0.167 m³/(h*L) the ash concentration after approx. 1600 hours would still remain at least one order of magnitude lower compared to the level of 3.4 g ESP ash/L, provided that just 1 mg/m³ particulate matter is absorbed. The dissolved Fe from absorbed particulate matter is expected to be approx. 0.5-1.0 mg/L under these conditions. For pilot plants with a higher specific enrichment factor of approximately 0.5 m³/(h*L) 2000 h are sufficient for 1 mg/m³ of absorbed particulate matter to accumulate 1 g/L which means dissolved Fe of 1-2 mg/L. After approximately 6000 h an ash concentration of 3.4 g/L is predicted. Demonstration or commercial CC plants with specific enrichment factors > 0.5 m³/(h*L) will require less operational hours compared to the CC pilot plants to achieve the same level for ash concentration or for dissolved Fe.

4. Conclusions/Recommendations

The results presented above lead to the following conclusions relevant for the investigations of CC processes at pilot –scale and operation at demonstration-scale:

1. The particulate matter concentrations upstream and downstream the CC plant are a very important parameters which should be determined regularly and considered thoroughly.
2. Leaching of absorbed fly ash particles lead to a dissolved Fe concentration of approx. 1 mg/L when just 500 mg/L (1:2000 (g/g)) particulate matter is absorbed. This takes place at the start of a CC plant operation and is dependent on the absorbed particulate matter and the specific enrichment factor. The dissolved Fe and the even smaller concentration of the other trace elements like Mn, V, Cu and Mo might trigger the accelerated formation of degradation products (carboxylic acids, amides etc.)
3. Leaching begins to occur immediately. 24 hours are sufficient for the dissolution of the majority of the soluble part of the ash, thus the accumulated concentration of ash should be considered for calculations, not the residence time.
4. CC pilot plant operational campaigns of 500-1000 h duration are not sufficient for a reliable examination of MEA losses, formation of degradation products and as well emissions when the site specific enrichment factor is low (0.4-0.2 $m^3/(h*L)$).
5. Filtrations by cartridge filters or activated carbon beds effectively remove particulate matter, but do not avoid the accumulation of dissolved species due to leaching.
6. It is a necessity to minimize the particulate matter which enters the CC absorber and/or to remove absorbed particulate matter entirely from the solvent loop shortly after absorption.
7. There is still an urgent requirement for further research on the dependency of the suspended ash concentration to the formation of degradation products with laboratory experiments. This should be complemented by studying the impact of dissolved metal, e.g. Fe, concentrations on the formation of degradation products using the same laboratory apparatus and conditions.

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